Indian J. Phys. **71B** (5), 589–595 (1997)

IJP
— an international journal

The Raman spectra of antimony sulfochloride and antimony sulfobromide

J Marshell

Department of Physics, Loyola College,
Chennai-600 034, India

Received 5 February 1997, accepted 19 May 1997

Abstract : Thiohalides of structure SbSX where X is Cl or Br can be treated as a bent XYZ type molecule belonging to C_s symmetry The molecules have 3 a' modes of vibration with all of them being infrared and Raman active A complete vibrational assignment of the Raman spectra of SbSCl and SbSBr were made The force constants, vibrational mean square amplitudes and vibrational mean amplitudes for the two molecules are presented for the first time

Keywords : Raman spectra, thiohalides, molecular constants

PACS Nos. : 33.20 Ea, 33.20.Fb, 33 20.Tp

1. Introduction

There are twelve compounds of metal thiohalides with structure ABX where A is Sb or Bi, B is S or Se and X is Cl, Br, or I. All of these compounds have been prepared and except BiSeCl all the compounds are isostructural. The preparation of these compounds is described by Donges [1,2]. The structure of SbSBr [3] consists of pleated chains of Sb and S atoms between which lie Br^- ions as shown in Figure 1. An arrangement of this type is found in a number of oxides M_2O_3 and sulphides M_2S_3 and is closely related to the chain in Sb_2S_3. Each Sb atom has one S atom at 2.49 Å and two S atoms at 2.67 Å. Each S atom is similarly bonded to three Sb atoms. The bond angles around Sb are 84.1 and 96.3 [4]. The nearest neighbours of Br^- ions are two Sb atoms at 2.94 Å and one S atom at 3.46 Å. The structure of SbSX where X is Cl or Br is treated as XYZ type belonging to C_s symmetry and shown in Figure 2. The three fundamental modes of vibration are the Sb–S stretching, Sb–X stretching and the S–Sb–X bending all belonging to a' species.

Address for correspondence : AP 745, G-Block, Anna Nagar West, Chennai-600 040, India

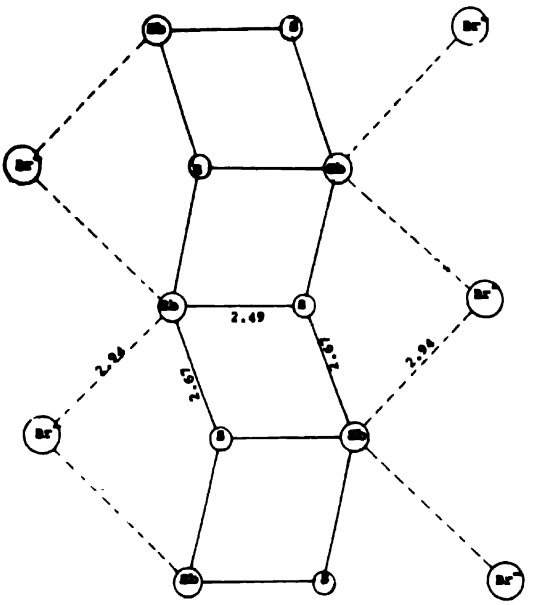

Figure 1. Structure of antimony sulfobromide.

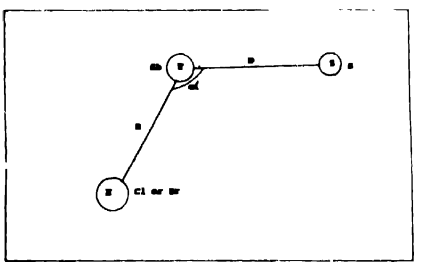

Figure 2. Geometrical configuration of the XYZ type of molecule.

2. Experimental

The Raman spectra of SbSCl and SbSBr recorded in the range 1300–50 cm^{-1} is presented in Figures 3 and 4 respectively. The sampling technique was KBr pellet. The probable assignments for SbSCl is in Table 1 and that of SbSBr in Table 2.

3. Result and discussion

3.1. Assignments:

The complete vibrational assignment of the three fundamentals, their potential energy distribution (P.E.D.) and overtone/combination for SbSCl and SbSBr is presented in Table 1 and Table 2 respectively. The Sb–S stretching frequency (ν_1) is assigned to 710 cm^{-1} for SbSBr and to 719 cm^{-1} for SbSCl both having a P.E.D. of 100 percent.

In $SbCl_3$ and $SbBr_3$ [5,6], the Sb–Cl stretching is assigned to a frequency at 376 cm^{-1} and Sb–Br stretching to 248–222 cm^{-1}. In SbSBr, the ν_2 stretching frequency corresponding to Sb–Br is assigned to 225 cm^{-1} and in SbSCl, it is assigned to 319 cm^{-1} each having a P.E.D.

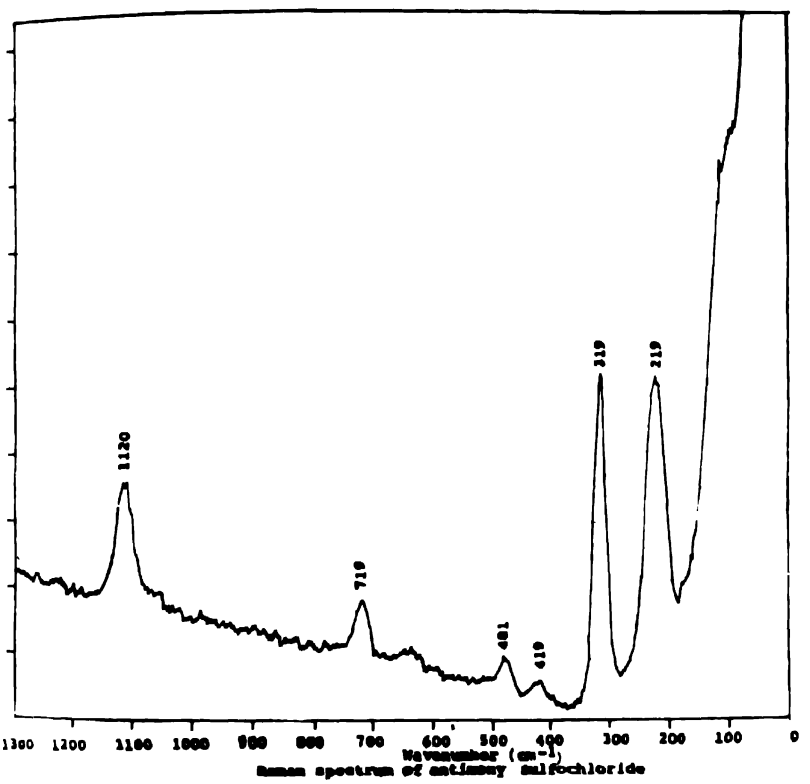

Figure 3. Raman spectrum of antimony sulfochloride

of 100 percent. In SbSBr, the ν_3 frequency is at 148 cm^{-1} with P.E.D. 93% and 219 cm^{-1} in SbSCl with P.E.D. 98%. In the Raman spectrum of SbSBr, the absorption at 186 cm^{-1} is a bending fundamental mode due to the conformation of the molecule. In the crystal structure of SbSBr [4], there are two bond angles around Sb atom indicating a change in structure or conformation of the molecule. Such conformational behaviour is exhibited in the structure of disulfur halides (S_2X_2) *viz.* disulfur chloride and disulfur bromide [7,8] and in alkyl monohalides belonging to C_s point group of symmetry which have two CCX deformation fundamentals. In the Raman spectrum of S_2Br_2, there are two fundamentals corresponding to the angle of deformation SSBr at 170 cm^{-1} and 199 cm^{-1} occurring with high intensity [7] which accounts for the high intensity bending fundamentals seen in the spectrum of SbSBr. The low frequency absorption of high intensity at about 75 cm^{-1} in

the specturm of SbSBr can be assigned to the torsional vibration of the molecule. This assignment agrees with the assignment in S_2Br_2 where the torsional mode is placed at

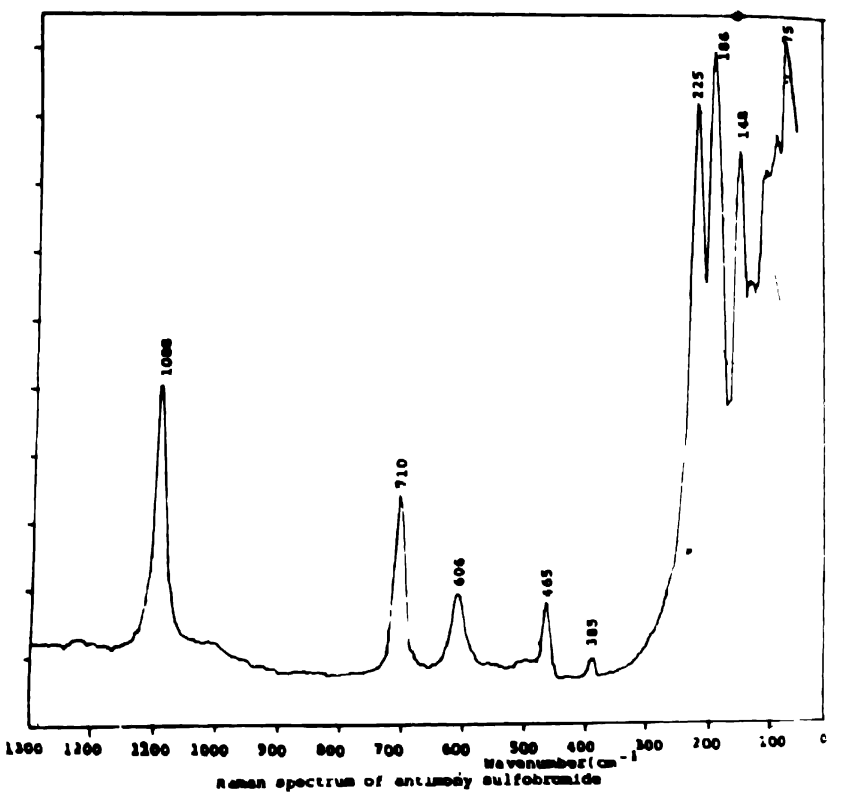

Figure 4. Raman spectrum of antimony sulfobromide

70 cm^{-1} and in S_2Cl_2 at 102 cm^{-1} occurring with high intensity comparable with the symmetric bending deformation vibration [8].

Table 1. Vibrational assignment of antimony sulfochloride.

Frequency (cm^{-1})	Assignment
1120	2 × 719 – 319 (FR)
719	Sb–S stretching (ν_1)
481	719 – 219
419	719 – 319
319	Sb–Cl stretching (ν_2)
219	S–Sb–Cl bending (ν_3)

FR – Fermi resonance

Table 2. Vibrational assignment of antimony sulfobromide

Frequency (cm^{-1})	Assignment
1088	710 + 225 + 148
710	Sb–S stretching (ν_1)
606	2 × 225 + 148 (FR)
465	710 – 225
385	225 + 148
225	Sb–Br stretching (ν_2)
186	S–Sb–Br bending
148	S–Sb–Br bending (ν_3)
75	Torsion

FR – Fermi resonance

In the Raman spectrum of SbSBr and SbSCl, no overtone band is present but a combination of overtone with the fundamental is seen and having higher intensity than the stretching fundamental vibration. The 1120 cm^{-1} band in SbSCl and the 606 cm^{-1} band in SbSBr are suspected to be Fermi resonance (FR) type interactions. The 1120 cm^{-1} band in SbSCl shows a fine split in its peak position while the 606 cm^{-1} band in SbSBr occurs close to the stretching fundamental frequency (ν_1). The other remaining bands were a combination of the fundamentals.

3.2 *Molecular constants* :

Many molecules of the type XYZ belonging to C_s symmetry has been investigated by previous workers [9–14]. The force constants for the molecules were calculated by solving Wilson's secular equation [15] using the kinetic constant method. Molecular kinetic constants are the vibrational inertia coefficients involved in Wilson's expressions for the kinetic energy relating to molecular vibrations given by $2T = \dot{S}' G^{-1} \dot{S}$, where $G^{-1} = K$. The elements of the matrix K are the kinetic constants. The symmetric kinetic constants are related to the symmetric force constants through the expression

$$\frac{F_{ij}}{F_{jj}} = \frac{K_{ij}}{K_{jj}} \qquad (i < j)$$

The force constants calculated for SbSCl and SbSBr is summarised in Table 3. The Sb–Br force constant is 1.424 and is in good agreement with the force constant of trihalides $SbBr_3$ where it is 1.5 1 mdyne/Å [16] and is usually in the range 1.34 – 1.69 mdyne/Å [5]. In SbSCl the Sb–Cl force constant is 1.63 and is around 2.0 in $SbCl_3$ [6]. Venkateswarlu [17] has calculated the Sb–Cl force constant in $SbCl_3$ to be 1.78. The Sb–S stretching force constant is 7.53 in SbSBr and 7.68 in SbSCl. All the interaction constants are within range. Using the symmetrized vibrational mean square amplitudes, Σ-matrix $\Sigma = L\Delta L'$ where L is the transformation matrix from normal co-ordinates to symmetry co-ordinates and $\Delta = \frac{h}{8\pi^2 c\nu_i} \coth(hc\nu_i/2kT)$. The bonded valence vibrational mean square amplitudes

for SbSCl and SbSBr is given in Table 4. The vibrational mean amplitudes both bonded and non-bonded for the two molecules were calculated.

Table 3. Force constants in SbSBr and SbSCl (10^{-2} N/m).

Force constant	SbSBr	SbSCl
f_D	7.526	7.676
f_R	1.424	1.630
f_α	0 216	0.371
f_{DR}	0.022	0 034
$f_{D\alpha}$	0 018	0 038
$f_{R\alpha}$	0.052	0 045

Table 4. Vibrational mean square amplitudes (10^{-3} A^{02}) and mean amplitudes (10^{-2} A^0) of SbSBr and SbSCl.

Mean square amplitudes	SbSBr	SbSCl
σ_D	1 0882	1.0745
σ_R	3.1900	3.0467
σ_α	0.3109	0.2202
σ_{DR}	–0.0237	–0.0234
$\sigma_{D\alpha}$	–0.0274	–0 0295
$\sigma_{R\alpha}$	–0 1703	–0 0947
Mean amplitudes		
U_{XY}	5 6483	5.5197
U_{YZ}	3.2987	3.2779
$U_{(X \quad Z)}$	10.0140	8.9534

4. Conclusion

There is limited literature on structure and spectroscopic details of metal thiohalides of type ABX where A is Sb or Bi, B is S or Se and X is Cl, Br or I. A complete vibrational assignment of the Raman spectra for SbSCl and SbSBr has been done assuming C_s symmetry point group. The correctness of the assignment was checked by calculating the P.E.D. using the force constants for the frequencies assigned. A complete set of potential force constants for the two molecules is presented. The mean square amplitudes and mean amplitudes of vibration for the two molecules were evaluated and their values are within acceptable range.

References

[1] E Donges Z. *Anorg. Chem.* **263** 112 (1950a)

[2] E Donges Z. *Anorg. Chem.* **263** 280 (1950b)

[3] G D Christofferson and J D McCullough *Acta Cryst.* **12** 14 (1959)

[4] N W Tideswell, F H Kruse and J D McCullough *Acta Cryst.* **10** 99 (1957)

[5] Philip W Davis and Robert Oetjen *J. Mol. Spectrosc.* **2** 253 (1958)

[6] Robin J H Clark and David M Rippon *J. Mol. Spectrosc.* **52** 58 (1974)

[7] E B Bradley, C A Frenzel and M S Mathur *J. Chem Phys* **49** 2344 (1968)

[8] E B Bradley, M S Mathur and C A Frenzel *J. Chem Phys* **47** 4325 (1967)

[9] E D Palik *J. Chem. Phys* **23** 280 (1955)

[10] S R Polo and M K Wilson *J. Chem. Phys.* **22** 900 (1954)

[11] D N Magnuson *J Chem. Phys* **19** 1071 (1951)

[12] P J Woltz, E A Jones and A H Wielson *J. Chem. Phys* **20** 378 (1952)

[13] L J Landau *J. Mol. Spectrosc.* **4** 276 (1960)

[14] W G Burns and H J Bernstein *J Chem. Phys.* **18** 1669 (1950)

[15] E B Wilson, J C Decius and P C Cross *Molecular Vibrations* (New York . McGraw Hill) (1955)

[16] E F Gross and I M Ginsburg *Opt. Spectrose* **1** 710 (1956)

[17] K Venkateswarlu and S Sundaram *Proc Phys Soc. (London)* **A69** 180 (1956)